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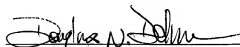
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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

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TITLE OF THE INVENTION (280 characters max)				
CATALYSTS FOR OLIGOMERIZATION OF ETHYLENE				
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CATALYSTS FOR OLIGOMERIZATION OF ETHYLENE

Background of the Invention

This invention relates generally to the preparation of trimers, tetramers, and polymers of ethylene catalyzed by derivatives of certain metal complexes.

The selective trimerization of ethylene to prepare primarily 1-hexene, and ultimately to form polymers therefrom, has been extensively studied and a number of catalysts developed. Examples include the well known chromium pyrrolide complexes, disclosed in U.S. Patents 5,523,507, 5,786,431, and elsewhere; trialkylsilylamide-chromium (II) complexes on activated inorganic refractory compounds in combination with aluminum trialkyl compounds, disclosed in U.S. Patent 5,104,841; chromium diphosphines, disclosed in Chem. Comm. (2002) p 858; chromium cyclopentadienyl catalysts as disclosed in Angew. Chem. Int. Ed. 38 (1999), p 428, J. Poly. Sci., 10 (1972), p2621, and Applied Catalysis A: General 255, (2003), p355-359; silica supported trialkylsilylamide- chromium complexes in combination with isobutylalumoxane, disclosed in J. Mol. Cat. A: Chemical, 187, (2002), p 135-141; mixed heteroatomic compounds disclosed in Chem. Comm. (2003), p 334; tantalum compounds disclosed in Angew. Chem. Int. Ed., 42, (2003), p808-810; titanium cyclopentadiene catalysts such as those of Angew. Chem. Int. Ed., 40, (2001), p2516; and numerous others. In U.S. Patent 5,137,994, a process for producing ethylene/1-hexene copolymers directly from ethylene using silica supported chromium compounds was disclosed. Control of polymer density was obtained by adjusting the ethylene/ 1-hexene ratio of the intermediate monomer mixture obtained in an initial trimerization.

Oligomerization and polymerization of higher olefins such as propylene and 1-butene is disclosed in U.S. Patent 4,668,838. The general mechanism of trimerization is considered to involve metalloheptane ring formation and most likely agnostic assisted hydride transfer, as disclosed in Angew. Chem. Int. Ed., 42, (2003), 808-810. The foregoing processes are highly useful for the selective formation of trimers in the substantial absence of higher oligomer or polymer formation. There remains a need for the discovery of processes for the selective formation of tetramers, especially 1-octene from ethylene.

Stepwise ethylene chain growth on aluminum alkyls was discovered in the 1950's by K. Ziegler et al. The reaction proceeds thermally at temperatures in the range of 100°-200° C. under high ethylene pressure, typically 2000-4000 psi (14-28 MPa). At higher temperatures, a displacement reaction or cracking step competes with chain growth, producing α -olefins and regenerating aluminum alkyl compounds. For a review see, "Comprehensive Organometallic Chemistry: 1982, Pergamon Press, Vol. 7, Section 46. The process may be advanced by catalysts both for the step-wise growth of the aluminum alkyl and the catalyzed displacement of α -olefins therefrom. Ziegler-Natta catalysts such as those discovered by Kaminsky et al. Angew. Chem. Int.

Ed. Engl., 1976, Vol. 15, pages 630-632 may be used to catalyze the growth process. This process is thought to involve active transition metal catalysts which promote the growth of the aluminum alkyl chains. Chain growth is terminated in the displacement or cracking step, principally by β -hydrogen or β -alkyl elimination to give a vinylic end group or by hydrogenolysis to give a paraffinic end group, thereby regenerating a catalytically active transition metal hydride or alkyl and an aluminum hydride or alkyl.

The manufacture of α -olefins using the foregoing step addition to aluminum alkyls is commercially practiced in large volume. Suitable processes operating at lower temperatures and pressures than those employed by early artisans are disclosed in U.S. Patent 5,276,220 (using actinide metal metallocene based complexes, which unfortunately are radioactive, as catalysts) and in U.S. Patent 5,210,338 (using metallocene based complexes of zirconium and hafnium).

A persistent problem of the foregoing step growth processes is the production of aluminum alkyls and the resulting α -olefin products having a narrow molecular weight distribution (Poisson distribution). In many such processes, the products are undesirably broad, and best described by the Schulz-Flory statistical distribution. These statistical distributions are commonly known and defined by the equations: Poisson: $X_p = (x^p \cdot e^{-x})/p!$, and Schulz-Flory: $X_p = \beta(1+\beta)^{-p}$, where X_p is the mole fraction with p added monomer units, x is the Poisson distribution coefficient equal to the average number of monomers added, and β is the Schulz-Flory distribution coefficient. A typical Schulz-Flory distribution of α -olefins would provide a maximum of 15 percent 1-hexene and 17 percent 1-octene. Additionally, significant quantities of 1-decene and higher α -olefins (C_{12-30} α -olefins) are produced, along with low molecular weight waxy polymers.

Despite the advance in the art encompassed by the foregoing known processes, a process that operates at milder temperatures and pressures to produce primarily trimers (1-hexene) and tetramers (1-octene), especially in a Poisson type distribution, while limiting less valuable butene, C_{10-30} α -olefin, and low molecular weight polymer formation is still desired. The α -olefin products of the present process, especially 1-hexene and 1-octene are useful industrial chemicals employed to prepare alcohols and plastics, especially high molecular weight, linear low density, polyethylene.

Further desired is a process for preparing high molecular weight polymers and/or copolymers of ethylene and branch inducing α -olefins such as 1-hexene and/or 1-octene (linear low density polyethylene) directly from ethylene.

Summary of the Invention

In accordance with this invention there is provided an improved catalyst composition for the preparation of oligomeric derivatives of olefin monomers, especially ethylene, comprising a Group 6 metal amide complex or compound, a Group 12, 13 or 14 metal hydrocarbyl composition or compound, and a solid support comprising aluminum phosphate.

Also provided is an improved process for the preparation of oligomeric derivatives of olefin monomers, especially ethylene, comprising contacting the olefin monomer or a mixture of olefin monomers under oligomer formation conditions with a catalyst composition comprising a Group 6 metal amide complex or compound, a Group 12, 13 or 14 metal hydrocarbyl composition or compound, and a solid support comprising aluminum phosphate.

In a further embodiment, there is provided a process for preparing high molecular weight polyethylene and/or short chain branched copolymers of ethylene and one or more C_{6-8} α -olefins, preferably 1-octene, by the direct α -olefin formation and polymerization of ethylene with a catalyst composition comprising a Group 6 metal amide complex or compound, a Group 12, 13 or 14 metal hydrocarbyl composition or compound, and a solid support comprising aluminum phosphate.

In yet another embodiment of the invention there is provided a process for the catalytic oligomerization of ethylene to yield a mixture comprising a Poisson distribution of 1-hexene and 1-octene products, preferably a product mixture comprising greater than 10 percent 1-octene and less than 90 percent, preferably less than 80 percent, 1-hexene with less than 10 percent butene and C_{10-30} α -olefin, and optionally polymer. Preferred catalysts are those comprising a Group 6 metal amide complex or compound, a Group 12, 13 or 14 metal hydrocarbyl composition or compound, and a solid support comprising aluminum phosphate.

In a final embodiment of the invention there is provided a polymerization process wherein the foregoing mixture of olefins is polymerized to form a high molecular weight polymer with or without the addition of ethylene or other polymerizable comonomer, in the presence of the same or a different catalyst or catalyst mixture.

Brief Description of the Drawing

Figure 1 gives conversions as a function of ethylene pressure for products prepared in Example 1.

Detailed Description of the Invention

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, raw materials, and general knowledge in the art.

If appearing herein, the term "comprising" and derivatives thereof is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed

herein. In order to avoid any doubt, all compositions claimed herein through use of the term “comprising” may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, “consisting essentially of” if appearing herein, excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term “consisting of”, if used, excludes any component, step or procedure not specifically delineated or listed. The term “or”, unless stated otherwise, refers to the listed members individually as well as in any combination. Unless stated to the contrary conventional in the art or implicit from the context, all parts and percents are based on weight.

Examples of α -olefins suitable for chain growth herein include, but are not limited, to C_2 to

C_6 straight chain α -olefins or mixtures thereof, with ethylene being the preferred olefin.

Suitable Group 6 metal amide compounds for use as the catalyst component of the present invention correspond to the following formula: $M(NR^1_2)_rX_{v-r}$

wherein M is a Group 6 metal, especially chromium in the +3 formal oxidation state;

R^1 independently in each occurrence is an alkyl group of from 3 to 20 carbons, a cycloalkyl group of from 5 to 20 carbons, an aryl or alkylaryl group of from 6 to 20 carbons, or a tri(C_{1-20} hydrocarbylsilyl) group, and optionally two R^1 groups on the same or adjacent amide groups may be joined together thereby forming a heterocycloaliphatic ring, or an alkyl-, aryl-, cycloalkyl-, or trihydrocarbylsilyl- substituted derivative thereof;

X is an anionic ligand of up to 20 atoms not counting hydrogen, and optionally one or more X groups and/or one or more NR^1_2 groups may be joined together to form an aliphatic or aromatic ring,

r is a number greater than 0 and less than or equal to v, and

v is the valence of M.

Preferred R^1 groups include secondary or tertiary alkyl groups, aryl, alkylaryl, and trihydrocarbylsilyl groups of from 3 to 20 carbons, or two R^1 groups on a single amide together are a C_{5-12} alkylene group. Most preferably R^1 each occurrence is isopropyl, cyclohexyl or trimethylsilyl.

Preferred X groups include hydride, halide, hydrocarbyl, trihydrocarbylsilyl, hydrocarbyloxy, and trihydrocarbylsiloxy of up to 10 atoms not counting hydrogen, most preferably chloride or methyl.

Examples of suitable Group 6 metal amide compounds include chromium tris(bis(trimethylsilyl)amide), chromium tris(diisopropylamide), chromium tris(diphenylamide), chromium tris(di(2-methylphenyl)amide), chromium tris(dicyclohexylamide), and chromium tris(2,2,6,6-tetramethylpiperdyl). Preferred Group 6 metal amide compounds are chromium tris(bis(trimethylsilyl)amide) and chromium tris(diisopropylamide). The group 6 metal amide compounds may be readily prepared by reaction of the corresponding trialkyl chromium compound with the lithium amide in an ether solvent followed by recovery from an aliphatic hydrocarbon, by

the technique previously disclosed in J.C.S., Dalton, (1972), p1580-1584, or by any other suitable technique. Highly desirably, the metal complex and the subsequent oligomerization or polymerization reaction is substantially devoid of Lewis base compounds such as ethers.

Mixtures of metal complexes of the foregoing type or mixtures thereof with other metal complexes may be employed if desired. In the manufacture of polymers mixtures of metal complexes are preferably employed. In this manner, a catalyst that is most efficient for producing oligomers may be employed in combination, either in a separate reactor or the same reactor, with a catalyst that is most efficient in producing copolymer products to optimize the formation of copolymeric products. Examples of suitable secondary metal complexes for use herein include the well known metallocene and constrained geometry titanium based metal complexes disclosed in U.S. Patents 6,268,444, 5,965,756, 5,703,187, 5,866,704, 6,150,297, 6,555,634, 6,515,155, 6,613,921, and elsewhere.

Suitable Group 12, 13 or 14 metal hydrocarbyl compounds for use herein especially include aluminum, zinc and tin compounds containing one or more hydrocarbyl ligand groups containing from 1 to 20 carbons in each hydrocarbyl group. Examples include trihydrocarbyl aluminums, dihydrocarbyl aluminum hydrides, dihydrocarbyl aluminum halides, dihydrocarbylaluminum hydrocarboxides, dihydrocarbyl zincs, tetrahydrocarbyl tins, alumoxanes, and mixtures thereof. Specific non-limiting examples of suitable aluminum hydrocarbyl compounds (which are the preferred a Group 12, 13 or 14 metal hydrocarbyl compound) include trialkylaluminum compounds such as triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, triisopropylaluminum, triisobutylaluminum, and the like, and alumoxanes such as methylalumoxane or triisobutylaluminum modified methalumoxane. Most highly preferred aluminum hydrocarbyl compounds are triethylaluminum (TEA), triisopropylaluminum (TIPA), and tri-isobutylaluminum (TIBA).

Suitable alumoxanes for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane, triisobutyl aluminum modified methylalumoxane, or isobutylalumoxane; neutral Lewis acid modified polymeric or oligomeric alumoxanes, such as the foregoing alkylalumoxanes modified by addition of a C₁₋₃₀ hydrocarbyl substituted Group 13 compound, especially a tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compound, or a halogenated (including perhalogenated) derivative thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially a perfluorinated tri(aryl)boron compound or a perfluorinated tri(aryl)aluminum compound.

Suitable supports comprise crystalline, semi-crystalline, and amorphous aluminum phosphate compounds, preferably highly amorphous aluminum phosphate. By the term "amorphous" is meant that the compound contains less than 60 percent preferably less than 50 crystallinity as determined by NMR or other suitable technique. Suitable aluminum phosphate

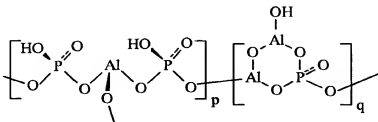
materials may be prepared substantially according to the technique disclosed by Glemza, et al., ACS Symposium on Catalyst Supports: Chemistry, Formation and Characterization, Div. of Petroleum Chemistry, New York, Aug. 25-30, 1991, *Catalysis Today*, 14 (1992) 175-188, EP-A-215,336 as well as U.S. Patents 6,461,415 or 6,036,762, by contacting a solution of an aluminum salt, especially aluminum nitrate, with a phosphorous containing compound such as phosphorus pentoxide, $\text{Na}_2\text{H}_2\text{PO}_5$, or phosphoric acid, forming a gel and removing the solvent. The aluminum phosphate may also be deposited as a surface coating on a solid substrate, especially a porous substrate such as silica or alumina, if desired. Generally, treatment of the aluminum phosphate with ammonia or other extracting agent, leads to higher amounts of polymer formation.

Desirably, the amount of surface hydroxyl functionality of the resulting aluminum phosphate material is reduced to as low as possible by thoroughly drying or calcining the product prior to use. Suitable drying or calcining conditions include heating the material to a temperature from 100 to 600°C for time periods from several minutes to several hours. Longer drying times are employed at lower drying temperatures.

Suitable aluminum phosphate compounds are those of the formula: $(\text{P}_2\text{O}_5)(\text{Al}_2\text{O}_3)_u$, wherein u is a number from 0.1 to 10. Nominal quantities of surface hydroxyl groups may be present on the aluminum phosphate surface, without substantial adverse consequence. Preferably the quantity of surface hydroxyl functionality is less than 10 ppm, most preferably less than 1.0 ppm.

Preferred aluminum phosphate compounds are those of the formula: $\text{Al}_x\text{P}_y\text{O}_4$ where $x+y=2$ and x is > 0.2 . Highly preferred compounds are those having a P/Al molar ratio from 0.6 to 1.0, preferably from greater than 0.90 to 1.0, and most preferably from 0.92 to 1.0. Compounds having higher P/Al molar ratio, especially ratios or approximately 1, are generally less crystalline or contain occluded crystalline regions thereby increasing the surface area and making them less subject to polymorphic transformations.

Most preferred aluminum phosphate compounds are substantially amorphous, three dimensional complexes corresponding to the formula:



wherein p and q are each independently numbers from 1-100, preferably from 1 to 5. Greater degrees of calcination can result in more complete removal of hydroxyl functionality and formation of additional oxygen bridges between neighboring phosphorous and/or aluminum atoms.

Desirably, the aluminum phosphate has a particle size from 10 to 1000 μm , preferably from 50 to 500 μm . Highly desirably, the aluminum phosphate is essentially or mostly amorphous and has a surface area from 100 to 500 m^2/g , more preferably from 200 to 350 m^2/g , a pore volume from 0.75 to 2.0 cm^3/g , more preferably from 1.0 to 1.5 cm^3/g , and a relatively large average pore size, preferably greater than 8.5 nm, more preferably greater than 10.0 nm, and most preferably greater than 15.0 nm.

The foregoing Group 6 metal complexes are activated to form the actual catalyst composition by combination with the hydrocarbylaluminum compound, and the support. The oligomerization process is conducted in the presence of the monomer to be oligomerized and optionally a diluent. Suitable diluents include liquid hydrocarbons such as C_{6-10} alkanes or cycloalkanes, and mixtures thereof. Additional additives, such as a chain transfer agent, e.g., hydrogen, used to control polymer chain length if polymerization is desired, may be present in the reaction as well, but are generally unnecessary. The resulting olefin products essentially follow the Poisson statistical distribution, generally comprising primarily trimer and tetramer products, and the process is characterized by low temperatures and pressures.

Desirably the process results in production of an olefin mixture comprising 1-hexene and 1-octene in which the weight ratio of 1-octene/1-hexene + 1-octene is greater than 20 percent, preferably greater than 25 percent. Additionally preferably, the weight ratio of 1-hexene + 1-octene to total alpha olefin reaction products is greater than 90 percent, more preferably greater than 95 percent. Highly desirably the quantity of polymer formed in the process is less than 60 percent of all products formed, preferably less than 50 percent.

Reaction temperatures for the oligomerization and polymerization process may vary from 20° to 150°C., preferably from 30°C to 120°C. Use of higher temperatures tends to increase polymer formation. Preferred temperatures for forming mixtures consisting primarily of ethylene oligomers, especially 1-hexene and 1-octene are from 20 to 80 °C, more preferably from 45 to 75 °C.

Pressures in all of the foregoing processes may be varied from 10 to 1000 psig (70 kPa to 7 MPa), preferably from 20 to 500 psi (150 kPa to 3.4 MPa). Suitably, the quantity of ethylene is employed to control reactor pressure. The mole ratio of catalyst composition (based on amount of Group 6 metal) to aluminum hydrocarbyl compound may be varied from 0.01:1 to 10:1, preferably from 0.05:1 to 1:1, and more preferably is in the range from 0.1:1 to 0.5:1. The amount of aluminum phosphate employed is desirably equivalent to or in excess of the amount of Group 6 metal compound used. Generally molar ratios based on Group 6 metal compound from 1:1 to 1×10^6 :1 are employed.

Where used, the mole ratio of aluminoxane to Group 6 metal complex, expressed as moles of total aluminum in the aluminoxane, may range from about 5/1 at high catalyst concentrations to

about 50,000/l at low catalyst concentrations. The various components of the catalyst composition may be added entirely at the initiation of the process, in portions throughout the reaction, or continuously, such as by means of a pump, through out the reaction. Highly desirably, the aluminum phosphate is added to the reactor or otherwise contacted with the Group 6 metal compound prior to addition of the aluminum hydrocarbyl compound. Intermittent or continuous addition of aluminum hydrocarbyl compound may prolong the catalyst lifetime.

It may be helpful under some operating conditions to pre-activate the catalyst in order to avoid an induction period. In one method, the catalyst is heated to 60-120°C in the presence of the aluminum phosphate compound prior to addition of the hydrocarbyl aluminum compound and olefin. A suitable period for such pretreatment is from 1 to 10 minutes. In another method, the catalyst and aluminum phosphate mixture is incubated in a solution of the hydrocarbyl aluminum compound, suitably at a temperature from 20 to 50°C, prior to addition of the olefin. In this method a suitable incubation period is from one minute to 20 minutes. According to either method, uptake of olefin occurs rapidly upon contacting with the active catalyst composition.

A diluent or solvent may be used in the process if desired. Preferred diluents or solvents include aliphatic or aromatic hydrocarbons, especially toluene, C₅₋₁₀ alkanes or cycloalkanes or mixtures thereof, and C₂₋₈ olefins, especially the olefin used as the addition monomer. A most preferred diluent is heptane.

The oligomeric α -olefin product can be recovered and separated by normal means such as fractionation. Alternatively, the oligomeric products can be oxidized and hydrolyzed in situ using known procedures to produce primary alcohols or hydrogenated to produce highly pure alkanes. Polymeric products, if any, are recovered by filtration or devolatilization. Highly desirably, the oligomeric product contains a large quantity of hexene and/or octene. In one embodiment of the invention 1-octene is prepared in high selectivity. That is, the quantity of octene in proportion to total octene and hexene is 30 percent or greater. The productivity of the catalyst compositions is measured in terms of turnovers, or number of ethylene units incorporated into the resulting product. Preferably, turnovers to hexene and octene are at least 300/hr and 150/hr respectively. If a polymeric product is desired, high turnover rates to polymer (greater than 500/hr) are desired as well. Most preferably the polymer incorporates significant quantities of hexene or octene, desirably at least 0.1 units per 1000 carbons total, more desirably at least 0.5 units per 1000 carbons total.

Polymerization, if conducted, is desirably carried out as a continuous polymerization, in which catalyst components, ethylene, and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to the reaction zone and polymer product continuously removed there from. Within the scope of the terms "continuous" and "continuously" as used in this context are those processes in which there are intermittent additions of reactants and removal of products at small regular intervals, so that, over time, the overall process is continuous.

The catalyst compositions can be advantageously employed in a high pressure, solution, slurry, or gas phase polymerization process alone or in combination with any suitable olefin polymerization catalyst. For a solution polymerization process it is desirable to employ homogeneous dispersions of the catalyst components in liquid diluent in which the polymer is soluble under the polymerization conditions employed. One such process utilizing an extremely fine silica or similar dispersing agent to produce such a homogeneous catalyst dispersion where either the metal complex or the cocatalyst is only poorly soluble is disclosed in U.S. Patent 5,783,512. A high pressure process is usually carried out at temperatures from 100°C to 400°C and at pressures above 500 bar (50 MPa). A slurry process typically uses an inert hydrocarbon diluent and temperatures of from 0°C up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerization medium. Preferred temperatures in a slurry polymerization are from 30°C, preferably from 60°C up to 115°C, preferably up to 100°C. Pressures typically range from atmospheric (100 kPa) to 500 psi (3.4 MPa).

Preferably for use in gas phase polymerization processes, the support material and resulting catalyst has a median particle diameter from 20 to 200 μm , more preferably from 30 μm to 150 μm , and most preferably from 50 μm to 100 μm . Preferably for use in slurry polymerization processes, the support has a median particle diameter from 1 μm to 200 μm , more preferably from 5 μm to 100 μm , and most preferably from 10 μm to 80 μm .

The catalyst composition of the present invention can also be employed to advantage in a gas phase polymerization process. Such processes are used commercially on a large scale for the manufacture of polypropylene, ethylene/ α -olefin copolymers, and other olefin polymers. The gas phase process employed can be, for example, of the type which employs a mechanically stirred bed or a gas fluidized bed as the polymerization reaction zone. Preferred is the process wherein the polymerization reaction is carried out in a vertical cylindrical polymerization reactor containing a fluidized bed of polymer particles supported or suspended above a perforated plate or fluidization grid, by a flow of fluidization gas.

The gas employed to fluidize the bed comprises the monomer or monomers to be polymerized, and also serves as a heat exchange medium to remove the heat of reaction from the bed. The hot gases emerge from the top of the reactor, normally via a tranquilization zone, also known as a velocity reduction zone, having a wider diameter than the fluidized bed and wherein fine particles entrained in the gas stream have an opportunity to gravitate back into the bed. It can also be advantageous to use a cyclone to remove ultra-fine particles from the hot gas stream. The gas is then normally recycled to the bed by means of a blower or compressor and one or more heat exchangers to strip the gas of the heat of polymerization.

A preferred method of cooling of the bed, in addition to the cooling provided by the cooled recycle gas, is to feed a volatile liquid to the bed to provide an evaporative cooling effect, often

referred to as operation in the condensing mode. The volatile liquid employed in this case can be, for example, a volatile inert liquid, for example, a saturated hydrocarbon having 3 to 8, preferably 4 to 6, carbon atoms. In the case that the monomer or comonomer itself is a volatile liquid, or can be condensed to provide such a liquid, this can suitably be fed to the bed to provide an evaporative cooling effect. The volatile liquid evaporates in the hot fluidized bed to form gas which mixes with the fluidizing gas. If the volatile liquid is a monomer or comonomer, it will undergo some polymerization in the bed. The evaporated liquid then emerges from the reactor as part of the hot recycle gas, and enters the compression/heat exchange part of the recycle loop. The recycle gas is cooled in the heat exchanger and, if the temperature to which the gas is cooled is below the dew point, liquid will precipitate from the gas. This liquid is desirably recycled continuously to the fluidized bed. It is possible to recycle the precipitated liquid to the bed as liquid droplets carried in the recycle gas stream. This type of process is described, for example in EP-89691; U.S. 4,543,399; WO-94/25495 and U.S. 5,352,749. A particularly preferred method of recycling the liquid to the bed is to separate the liquid from the recycle gas stream and to reinject this liquid directly into the bed, preferably using a method which generates fine droplets of the liquid within the bed. This type of process is described in WO-94/28032.

The polymerization reaction as well as α -olefin formation occurring in the gas fluidized bed is catalyzed by the continuous or semi-continuous addition of catalyst composition according to the invention. The catalyst composition may be subjected to a prepolymerization step, for example, by polymerizing a small quantity of olefin monomer in a liquid inert diluent, to provide a catalyst composite comprising supported catalyst particles embedded in olefin polymer particles as well.

The polymer is produced directly in the fluidized bed by polymerization of the monomer or mixture of monomers on the fluidized particles of catalyst composition, supported catalyst composition or prepolymerized catalyst composition within the bed. Start-up of the polymerization reaction is achieved using a bed of preformed polymer particles, which are preferably similar to the desired polymer, and conditioning the bed by drying with inert gas or nitrogen prior to introducing the catalyst composition, the monomers and any other gases which it is desired to have in the recycle gas stream, such as a diluent gas, hydrogen chain transfer agent, or an inert condensable gas when operating in gas phase condensing mode. The produced polymer is discharged continuously or semi-continuously from the fluidized bed as desired.

The gas phase processes most suitable for the practice of this invention are continuous processes which provide for the continuous supply of reactants to the reaction zone of the reactor and the removal of products from the reaction zone of the reactor, thereby providing a steady-state environment on the macro scale in the reaction zone of the reactor. Products are readily recovered by exposure to reduced pressure and optionally elevated temperatures (devolatilization) according to

known techniques. Typically, the fluidized bed of the gas phase process is operated at temperatures greater than 50°C, preferably from 60°C to 110°C, more preferably from 70°C to 110°C.

Uniquely in the present process, α -olefin formation can be induced and optimized in a separate step during the monomer recycle step. That is, a separate reactor and reaction conditions designed for maximum production of the present comonomers, can be inserted into what conventionally is merely a recycle and cooling loop of the gas phase reactor. A separate olefin polymerization catalyst, especially such a catalyst that is optimized for polymer formation or comonomer incorporation, can be used in the usual manner in the gas-phase polymerization reactor to produce polymer products from the olefin mixture produced from the recycled monomer stream. Alternatively, the two catalysts can be used as a mixture, if desired. Thus, according to the invention there is provided a process for preparing copolymers of ethylene and one or more C_{4-8} α -olefins by the direct α -olefin formation and polymerization of ethylene comprising contacting ethylene under oligomer formation conditions with a catalyst composition according to the invention and polymerizing, separately or in the same reactor, at least a portion of the resulting oligomers. Preferably, the process is one in which the ethylene source is recycle of monomer in an ethylene polymerization process.

Suitable gas phase processes which are adaptable for use in the process of this invention are disclosed in U.S. Patents: 4,588,790; 4,543,399; 5,352,749; 5,436,304; 5,405,922; 5,462,999; 5,461,123; 5,453,471; 5,032,562; 5,028,670; 5,473,028; 5,106,804; 5,556,238; 5,541,270; 5,608,019; and 5,616,661.

EXAMPLES

The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed. The following examples are provided as further illustration of the invention and are not to be construed as limiting. The term "overnight", if used, refers to a time of approximately 16-18 hours, the term "room temperature", refers to a temperature of about 20-25 °C, and the term "mixed alkanes" refers to a commercially obtained mixture of C_{6-9} aliphatic hydrocarbons available under the trade designation Isopar E[®], from Exxon Mobil Chemicals Inc. In the event the name of a compound herein does not conform to the structural representation thereof, the structural representation shall control.

The synthesis of all metal complexes and the preparation of all screening experiments are carried out in a dry nitrogen atmosphere using dry box techniques. All solvents used are HPLC grade and are dried before use.

Chromium (III) tris(bis(trimethylsilyl)amide) is synthesized substantially according to the technique of Bradley et al., J. Chem. Soc. Dalton, (1972) 1580-1584.

Amorphous aluminum phosphate (AlPO) is synthesized substantially according to the technique of Glenza, et al., ACS Symposium on Catalyst Supports: Chemistry, Formation and Characterization, Div. of Petroleum Chemistry, New York, Aug. 25-30 (1991).

5 Example 1

An automated pressure reactor comprising eight pressure cells with a working liquid volume of each cell of 6 mL is used to prepare ethylene oligomerization and polymerization products. The ethylene is polymer grade and is further purified by passing through an Oxyclear™ purifier (Labclear, Oakland CA) and a cylinder of activated molecular sieves (40 nm pore size). Each of the eight glass inserts is charged with 100 mg of AlPO having a particle size between 120 and 230 mesh (125-63 μm) and placed in a 200 °C oven overnight. The tubes are inserted into the pressure cells in the pressure reactor located in a dry box. To each tube is added sequentially 4.9 mL heptane and 0.8 mL of a solution of chromium (III) tris(bis(trimethylsilyl)amide) in heptane (0.01 M, 8 μmol Cr and 40 mg nonane internal standard). These mixtures are heated to 40 °C and stirred for 30 minutes. In all cases, the supernatant is a pale green color indicating incomplete deposition of the Cr compound. To each tube is then added 0.48 mL of a 0.05 M solution of TEAL in heptane (24 μmol, 3 eq.). The reactor head is put in place and each vessel heated to 70 °C before pressurizing with ethylene to various pressures. After suitable reaction times, the reactors are vented and the liquid analyzed by GC/MS. Solids are dried and weighed. Ethylene conversions as a function of pressure for hexene, octene and polymer and including a linear best fit (for pressures in psi) are shown in Figure 1.

Examples 2-5

The reaction conditions of Example 1 are substantially repeated using different hydrocarbyl aluminum compounds (trimethylaluminum (TMA), triisobutylaluminum (TiBA), triethylaluminum (TEAL) and triisobutylaluminum modified methylalumoxane (MMAO)) in a 4:1 molar ratio to chromium (III) tris(bis(trimethylsilyl)amide) catalyst. Reactions were conducted at 70 °C for 60 minutes. Essentially no 1-butene nor 1-decene were detected in the product mixture. Other product formation is calculated as turnovers/hour (TO) and shown in Table 1.

Table 1

Ex.	Al reagent	TO 1-hexene	TO 1-octene	TO polymer	percent polymer	octene/ octene+hexene
2	TMA	507	227	607	45	0.31
3	TiBA	481	235	839	54	0.33
4	TEAL	385	186	732	56	0.32
5	MMAO	375	163	714	57	0.30

Polymer produced from the reaction of Example 4 is analyzed to determine molecular weight and branching frequency. The result indicates a polymer having a bimodal molecular weight distribution with on average 1.64 butyl branches per 1000 total carbons.

CLAIMS

1. A catalyst composition for the preparation of oligomeric derivatives of olefin monomers, comprising a Group 6 metal amide complex or compound, a Group 12, 13 or 14 metal hydrocarbyl composition or compound, and a solid support comprising aluminum phosphate.

2. The catalyst composition of claim 1 wherein the Group 6 metal amide complex corresponds to the following formula: $M(NR^1)_2X_v$,
wherein M is a Group 6 metal;

R¹ independently in each occurrence is a secondary or tertiary alkyl group of from 3 to 20 carbons, a cycloalkyl group of from 5 to 20 carbons, an aryl or alkylaryl group of from 6 to 20 carbons, or a tri(C₁₋₂₀)hydrocarbylsilyl group, and optionally two R¹ groups on the same or adjacent amide groups may be joined together thereby forming a heterocycloaliphatic ring, or an alkyl-, aryl-, cycloalkyl-, or trihydrocarbylsilyl- substituted derivative thereof;

X is an anionic ligand of up to 20 atoms not counting hydrogen, and optionally one or more X groups and/or one or more NR¹₂ groups may be joined together to form an aliphatic or aromatic ring,

r is a number greater than 0 and less than or equal to v, and

v is the valence of M.

3. The catalyst composition of claim 1 wherein the Group 12, 13 or 14 metal hydrocarbyl composition or compound is triethylaluminum, triisopropylaluminum, or triisobutylaluminum.

4. The catalyst composition of claim 2 wherein the Group 12, 13 or 14 metal hydrocarbyl composition or compound is triethylaluminum, triisopropylaluminum, or triisobutylaluminum.

5. The catalyst composition of claim 1 wherein the aluminum phosphate is substantially amorphous and corresponds to the formula: $Al_xP_yO_4$ where $x+y=2$ and $x > 0.2$.

6. The catalyst composition of claim 5 wherein the aluminum phosphate has a P/Al molar ratio from 0.92 to 1.0.

7. A process for the preparation of oligomeric derivatives of olefin monomers, comprising contacting an olefin monomer or a mixture of olefin monomers under oligomer formation conditions with a catalyst composition according to claim 1.

8. The process of claim 7 wherein the olefin monomer is ethylene.

9. A process for the catalytic oligomerization of ethylene to yield a mixture comprising a Poisson distribution of 1-hexene and 1-octene products characterized in that the catalyst composition comprises a Group 6 metal amide complex or compound, a Group 12, 13 or 14 metal hydrocarbyl composition or compound, and a solid support comprising aluminum phosphate.

10. The process of claim 9 wherein the α -olefin product mixture comprises greater than 10 percent 1-octene and less than 90 percent 1-hexene, with less than 10 percent of all other α -olefin reaction products, and optionally polymer.

5 11. A process for preparing copolymers of ethylene and one or more C_{4-8} α -olefins by the direct α -olefin formation and polymerization of ethylene comprising contacting ethylene under oligomer formation conditions with a catalyst composition according to claim 1 and polymerizing at least a portion of the resulting oligomers.

12. A process according to claim 11 in which the ethylene source is recycle of monomer in an ethylene polymerization process.

10 13. A process according to claim 11 wherein a mixture of catalyst compositions or a second olefin polymerization catalyst is employed.

ABSTRACT

A catalyst composition for the preparation of oligomeric and/or polymer derivatives of olefin monomers, said composition comprising a Group 6 metal amide complex, an aluminum hydrocarbyl compound, and a solid support comprising aluminum phosphate.

Fig. 1

